

# Effect of Reaction Furnace and Converter Temperatures on Performance of Sulfur Recovery Units (SRUs)

Hamid Reza Mahdipoor, Keyvan Khorsand, Reza Hayati, Hooman Javaherizadeh

Department of Process and Equipment Technology Development, Research Institute of Petroleum Industry,  
West Blvd. of Azadi Stadium, Tehran, Iran  
mahdipoorhr@ripi.ir

**Abstract**-The modified Claus process is commonly used in oil refining and gas processing to recover sulfur and destroy contaminants formed in upstream processing. In oil refining, in addition to the typical modified Claus plant feed, i.e.  $H_2S$  and  $CO_2$ ,  $NH_3$ ,  $CS_2$ , and  $COS$  are also often present or formed. These contaminants pose a risk of poisoning the catalyst beds, as well decreasing the overall sulfur recovery. In this paper, effect of reaction furnace and converter temperatures on performance of SRUs is described. Then, the common ways for adjusting these important parameters are presented for a typical sulfur recovery unit. The achieved results can be useful for designing the new Claus sulfur recovery units.

**Keywords**-Claus Process; Furnace and Converter Temperatures

## I. INTRODUCTION

The Claus process continues to be the most widely used process for the conversion of  $H_2S$  to sulfur [1]. The task of Claus processes is to recover elemental sulfur from hydrogen sulfide and, more generally, from byproduct gases originating from physical and chemical gas and oil treatment units in refineries, natural gas processing, and gasification plants, to quote a few [2]. They consist of a thermal reaction furnace, a waste heat boiler, and a series of catalytic reactors (converters) and condensers (Figure 1). The reactions occurring in the furnace are numerous, and several authors have attempted to delineate the important ones [3-6]. The overall reaction characterizing the process is as follows [2]:

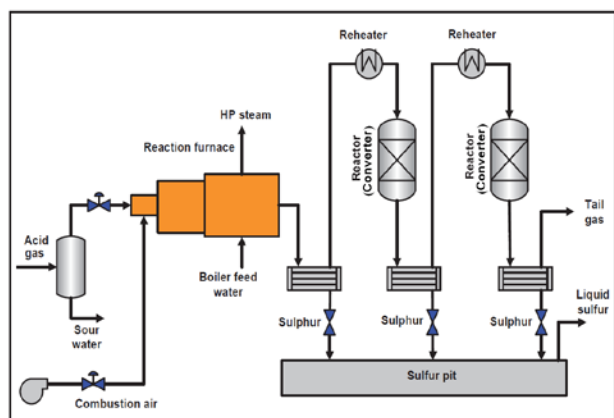
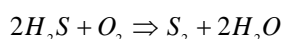
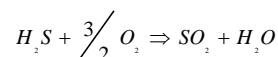


Fig. 1 The schematic shape of a typical Claus unit

In the first step or thermal stage, one-third of the  $H_2S$  is completely oxidized to  $SO_2$  in the reaction furnace, locating at the front end of plant. A benefit that also occurs is the production of significant quantities of elemental sulfur ( $S_2$ ) from the thermal decomposition of  $H_2S$ . In fact, the sulfur

produced in the furnace is 50-60% of the total sulfur condensed in the plant. The main  $H_2S$  oxidation reaction is [7],



The reaction furnace is followed by the waste heat boiler (WHB), where heat is recovered by cooling the furnace product gases [7]. In the second step that the catalytic stage, unreacted  $H_2S$  is then combined with  $SO_2$ , reacting via eq. 2, over an alumina catalyst to form elemental sulfur in fixed bed reactors by the following reaction [7,8],



Since this reaction is exothermic, decreasing the temperature leads the equilibrium reaction toward right hand, i.e. more sulfur yields. On the other hand, low temperatures decrease the reaction rate. Therefore, an appropriate catalyst must be used to increase the reaction rate. However, high sulfur yields still necessitate a multistage process with inter-stage cooling and sulfur condensation [8].

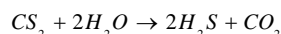
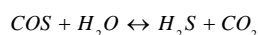
Sulfur formed in each stage of the Claus plant is condensed and recovered to achieve maximum conversion in the catalytic reactors. The unrecovered sulfur, in elemental or combined form ( $H_2S$ ,  $COS$ ,  $CS_2$ ), is combusted to  $SO_2$  in the tail gas incinerator which is then emitted to the atmosphere. Tail gas clean-up units are added sometimes prior to incineration to increase the sulfur recovery and minimize emissions [7].

One of the furnace functions is the destruction of any contaminants what may foul downstream equipments. In oil refinery operations,  $NH_3$  is formed as a byproduct what is then directed to the sulfur recovery facility for destruction [5]. Incomplete pyrolysis or combustion of  $NH_3$  in the furnace results in  $NH_3$  and  $NO$  carryover into the catalyst beds. Ammonia can form ammonium salts, which can plug or foul the catalyst beds, other equipments, or piping. Although the formation of  $SO_3$  occurs in the catalyst bed regardless of the presence of  $NO$ , the presence of  $NO$  in the beds acts as a catalyst for the conversion of  $SO_2$  to  $SO_3$ , which in turn causes catalyst sulfation [9]. Of the primary causes of catalyst activity loss, catalyst sulfation is regarded as the most significant [10]. It is therefore critical to convert as much  $NH_3$  to  $N_2$ ,  $H_2$ , and  $H_2O$  as possible.

For ammonia destruction, an empirical rule of thumb in industry is that furnace temperature should be greater than 1200-1250 °C [5]. The furnace temperature must be below the temperature limitation of conventional refractories of 1600°C and above the minimum stable furnace temperature of 926°C

[11]. The reaction furnace temperature should not exceed 1380 °C in order not to exceed the maximum temperature limitations of the equipment materials [12].

In the Claus process, other sulfur compounds will be formed, such as carbon disulfide (CS<sub>2</sub>) and carbon oxysulfide (COS), and these compounds can often contribute from 20 to 50% of the pollutants in the tail-gas [13,14]. Furthermore, presence of O<sub>2</sub> traces in the CS<sub>2</sub>-H<sub>2</sub>O mixture caused a decrease in the activity of alumina and titania catalysts due to sulfate formation [15]. Therefore, COS and CS<sub>2</sub> should be hydrolyzed in the catalytic converter [16, 17], as shown below:



The temperature of the first catalytic reactor is maintained at about 350°C to hydrolyze COS and CS<sub>2</sub>, while that of the subsequent reactors is just above the sulfur vapor dew point [18]. Transition metal oxides can be used to modify gamma-alumina to form a catalyst that is effective at temperatures higher than the dew point of sulfur [19-21]. However, thermodynamics provide a strong incentive to operate the catalytic converters at low temperature [22, 23] as a lower temperature should increase the exothermic reaction efficiency. Therefore, the temperature of the process gas at the inlet of the catalytic converters should be such that the effluent gas temperature is about 14-17°C higher than the expected outlet sulfur dew point and high enough for hydrolysis of COS and CS<sub>2</sub> for the first catalytic converter only [24] (about 350°C).

In this paper, the temperature of reaction furnace of a typical Claus Sulfur Recovery Unit is adjusted to ensure suitable NH<sub>3</sub> destruction. Moreover, the inlet temperatures of SRU converters are determined such that the proper conversion can be achievable without any processing problems. The process temperatures are important in designing the Claus sulfur recovery units.

## II. SRU REACTION FURNACE

As mentioned before, since only one-third of H<sub>2</sub>S convert to SO<sub>2</sub> in the reaction furnace, the unreacted H<sub>2</sub>S and inert gases consume the released energy from this exothermic reaction and the furnace reach to a thermal equilibrium. It decreases the temperature of reaction furnace. For this reason, a split-flow reaction furnace design (Figure 2) is applied to process the gas streams containing considerable amounts of ammonia. In this method, all the combustion air and all the ammonia containing sour gas are mixed with a portion of the acid gas stream and inserted to the first zone of the furnace and the remaining acid gas is then mixed with the products of the combustion from the first zone in zone 2 of the reaction furnace [25,26].

For illustrating the split-flow method, the Claus unit of a typical refinery is considered. The SRU feedstock consists of 74 Kmol/h acid gas from amine sweetening unit at 46°C and 1.3 bar, together with 38 Kmol/h sour gas from sour water treating unit at 90°C and 1.5 bar. The molar compositions of these streams are presented in Table 1. The sour gas containing 275 Kg/h ammonia and therefore, the furnace temperature should increase, up to the ammonia destruction temperature. For this reason, a case study is performed in which the acid gas split into two zone. Figure 3 illustrates the achieved results. The horizontal axis indicates the ratio

between the flow rate of acid gas entered to zone 1 and the flow rate of acid gas entered to zone 2. The vertical axis represents the changes of the first zone temperature.

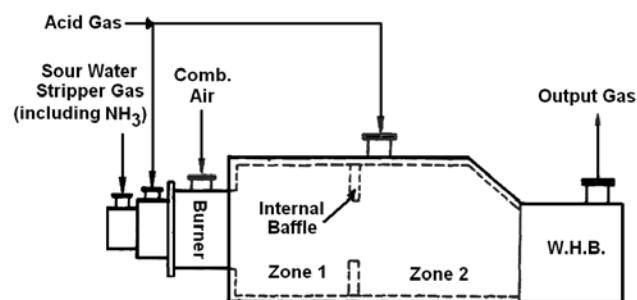


Fig. 2 A split-flow reaction furnace design

TABLE 1 THE COMPOSITION OF THE CLAU UNIT OF FEEDSTOCK

Component	Mole Fraction	
	Acid Gas	Sour Gas
H <sub>2</sub> S	91.6	24.3
H <sub>2</sub> O	7.3	33.2
C <sub>2</sub> H <sub>6</sub>	1.1	0
NH <sub>3</sub>	0	42.5

If combustible gases enter to the furnace first zone as their stoichiometric coefficients, the reaction furnace temperature will be maximized, for no excess gas or excess oxygen (excess air) is there. The maximum point of this curve is related to this condition. Before this point, the amounts of combustible gases (including H<sub>2</sub>S) are less than needed one-third of total H<sub>2</sub>S and therefore, temperature is decreased. Regarding to Figure 3, if the split-flow ratio was equal to 0.8, a temperature around 1350°C would be achievable for zone 1 of the reaction furnace. This temperature guaranties the complete destruction of NH<sub>3</sub>. If more expensive refractory with better resistance was applied, the furnace would be operate at higher temperatures by decreasing this ratio (see Figure 3).

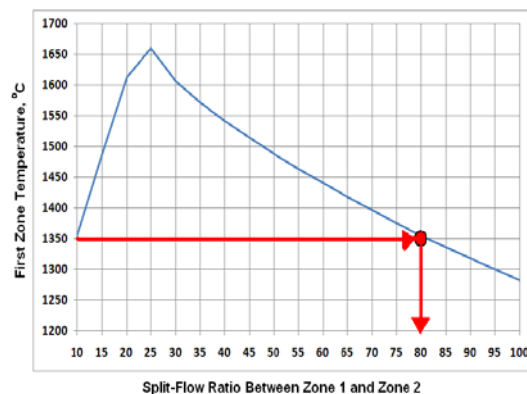


Fig. 3- A split-flow ratio between zone 1 and zone 2 vs. variations of zone 1 temperature

The operating problems related to the split-flow design including inadequate destruction of hydrocarbons and ammonia that might be contained in the bypassed portion of the acid gas and inadequate reaction of furnace residence time for thermal Claus sulfur conversion. The alternate way to overcome these problems is preheating the acid gas and combustion air and using high-intensity burners in the reaction furnace [11].

## III. SRU REACTORS (CONVERTERS)

The temperature of the process gas at the inlet of the catalytic converters should be such that the effluent gas

temperature is about 14-17°C higher than the expected outlet sulfur dew point. For this purpose, the outlet streams of two converters in the above plant are investigated. Table II presents pressure, temperature, and compositions of outlet streams of these converters. These data are achieved by the assumption of 265°C for temperature of the first converter inlet stream and 195°C for temperature of the second converter inlet stream.

TABLE II THE OUTPUT CONDITIONS OF CLAUS CONVERTERS

	Converter 1	Converter 2
Pressure (bar)	1.1	1.05
Temperature (°C)	310	225
Component (mass%)		
H <sub>2</sub> S	2.8	0.8
H <sub>2</sub> O	22.9	28.0
CO <sub>2</sub>	0.6	0.7
SO <sub>2</sub>	2.7	0.8
H <sub>2</sub>	0.2	0.2
N <sub>2</sub>	56.4	65.7
Sulfur	14.4	3.8

Figure 4 represents the variations of vapor phase fraction vs. outlet temperatures of two Claus reactors. According to this figure, dew point of the first converter outlet stream is equal to 253°C which is 57°C less than its assumed temperature from Table 2. With respect to criterion of 14-17°C, the temperature of 270°C seems to be appropriate for the outlet temperature of first converter. However, this temperature should be increased to ensure hydrolysis of COS and CS<sub>2</sub> in the first reactor. Therefore, the assumption of 265°C is a good value for the temperature of the first converter inlet stream. Furthermore, dew point of second converter outlet stream is equal to 210°C which is 15°C less than its assumed temperature value from Table II and takes the above criterion in the consideration.

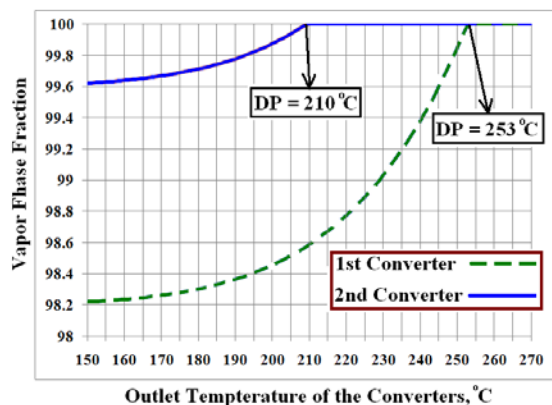


Fig. 4 The variations of vapor phase fraction vs. outlet temperatures of SRU reactors

#### IV. CONCLUSION

The modified Claus process was introduced as a commonly unit to recover sulfur and destroy contaminants formed in upstream processing. In these units, in addition to converting H<sub>2</sub>S to sulfur, other contaminants such as NH<sub>3</sub>, CS<sub>2</sub>, and COS must be eliminated. Rigorous adjustment of process temperatures is important to achieve this purpose. In this paper, the parameters that may affect adjusting the temperature of furnace and converters were investigated by means of analyzing a typical sulfur recovery unit. The achieved results illustrate a method which is useful for designing the new sulfur recovery units.

#### REFERENCES

- [1] Zare Nezhad, B., An investigation on the most important influencing parameters regarding the selection of the proper catalysts for Claus SRU converters, *J. Ind. Eng. Chem.* 15 (2009) 143-147.
- [2] Signor, S., Manenti, F., Grottoli, M. G., Fabbri, P., and Pierucci, S., Sulfur Recovery Units: Adaptive Simulation and Model Validation on an Industrial Plant, *Ind. Eng. Chem. Res.* 49 (2010) 5714-5724.
- [3] Hawboldt, K. A.; Monnery, W. D.; Svrcek, W. Y. A Study on the Effect of Quench Design on the Quality of Experimental Data. *Ind. Eng. Chem. Res.*, 38 (1999) 2260-2263.
- [4] Hawboldt, K. A.; Monnery, W. D.; Svrcek, W. Y. New Experimental Data and Kinetic Rate Expression for H<sub>2</sub>S Cracking and Re-Association. *Chem. Eng. Sci.* 55 (1999) 957-966.
- [5] Monnery, W. D., Hawboldt, K. A., Pollock, A. E. and Svrcek, W. Y., Ammonia Pyrolysis and Oxidation in the Claus Furnace, *Ind. Eng. Chem. Res.* 40 (2001) 144-151.
- [6] Clark, P. D., Dowling, N. I., Huang, M., Chemistry of the Claus Front-End Reaction Furnace. Hydrocarbon Reactions and the Formation and Destruction of CS<sub>2</sub>. Proceedings of the Brimstone Sulfur Recovery Symposium, Vail, CO, Sept (1997) 23-26.
- [7] Nasato, L. V., Karan, K., Mehrotra, A. K., and Behie, L. A., Modeling Reaction Quench Times in the Waste Heat Boiler of a Claus Plant, *Ind. Eng. Chem. Res.* 33 (1994) 7-13.
- [8] Elsner, M. P., Menge, M., Müller, C., Agar, D. W., The Claus process: teaching an old dog new tricks, *Catalysis Today* 79-80 (2003) 487-494.
- [9] Garside, J. E.; Phillips, R. F. Pure and Applied Chemistry; Pittman and Sons Ltd.: London, 1962.
- [10] Grancher, P. Advances in Claus Technology. *Hydrocarbon Process.* 1978, 57 (7), 155-160.
- [11] Kohl, A., Nielsen, R. B., Gas Purification, 5th ed., Gulf Publishing Company, Houston, Texas, 1997.
- [12] Sassi, M. and Gupta, A., K., Sulfur Recovery from Acid Gas Using the Claus Process and High Temperature Air Combustion (HiTAC) Technology, *American Journal of Environmental Sciences* 4 (2008) 502-511.
- [13] Gens, T.A., Decrease in Carbonyl Sulfide in the Feed to Claus Converters by Shift Catalysts, *Ind. Eng. Chem. Res.* 33 (1994) 1654-1656.
- [14] Huisman H.M., P. van der Berg, R. Mos, A.J. van Dillen, and J.W. Geus, Hydrolysis of Carbon Sulfides on Titania and Alumina Catalysts: The Influence of Water, *Applied Catalysis A*, 115 (1994) 157-172.
- [15] Laperdrix, E., I. Justin, G. Costentin, O. Saur, J.C. Lavalley, A. Aboulayt, J.L. Ray, and C. Nedez, Comparative Study of CS<sub>2</sub> Hydrolysis Catalyzed by Alumina and Titania, *Applied Catalysis B: Environment*, 17 (1998) 167-173.
- [16] Puchyr, D.M J., A.K Mehrotra, LA Behie, and N. Kalogerakis, Hydrodynamic and Kinetic Modeling of Circulating Fluidized Bed Reactors Applied to a Modified Claus Plant, *Chem. Eng. Sci.* 51 (1996) 5251-5262.
- [17] Maadah, A.G. and R.N. Maddox, Predict Claus Product, *Hydrocarbon Processing* 57 (1978) 143-146.
- [18] Burns, R.A., R.B Lippert, and R.K. Kerr, Choose Catalyst Objectively, *Hydrocarbon Processing*, 53 (1974) 181-186.
- [19] George, Z.M., Effect of Catalyst Basicity for COS, SO<sub>2</sub> and COS Hydrolysis Reactions, *J. catalysis*, 35 (1974) 218-224.
- [20] Terorde, R.J.A.M., PJ. van den Brink, L.M. Visser, A.J. van Dillen, and G.W. Geuss, Selective Oxidation of Hydrogen Sulfide to Elemental Sulfur Using Iron Oxide Catalysts on Various Supports, *Catalysis Today* 17 (1993) 217-224.
- [21] Berben, P.H., Ph.D. Thesis, University of Utrecht, The Netherlands, 1992.
- [22] Ledoux, M.J., P.H. Cuong, N. Keller, J.B. Nougayrede, S. Savin-Poncet, and J. Bousquet, Selective Oxidation of H<sub>2</sub>S in Claus Tail-Gas over SiC Supported NiS<sub>2</sub> Catalyst, *Catalysis Today* 61 (2000) 157-163.
- [23] Kerr, K.R., Energy Processing Canada, pp 28-35, July-August 1976.
- [24] Gas Processors Suppliers Association (GPSA). Engineering Data Book; GPSA Tulsa, 1987; Chapte.
- [25] Wiley, S., Off-gas aids Claus operations," *Hydro. Process.* 59 (1980) 127-129.
- [26] Chute, A. E., Tailor sulfur plants to unusual conditions, *Hydro. Process.* 56 (1977) 119-124.